UNIVERSITI PUTRA MALAYSIA

REMOVAL OF Cu (II) AND Cr(VI) FROM AQUEOUS SOLUTIONS BY WATER LILIES (*NYMPHAEA SPONTANEA*)

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REMOVAL OF Cu (II) AND Cr(VI) FROM AQUEOUS SOLUTIONS BY WATER LILIES (*NYMPHAEA SPONTANEA*)

By

CHOO TZE PEI

Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in Institute of Bioscience Universiti Putra Malaysia

June 2001

DEDICATED TO:

Beloved mum, dad, Jimmy, Johnny, teachers and friends

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

REMOVAL OF Cu(II) AND Cr(VI) FROM AQUEOUS SOLUTIONS BY WATER LILIES (*NYMPHAEA SPONTANEA*)

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June 2001

Chairman: Professor Lee Chnoong Kheng, Ph.D

Faculty: Science and Environmental Studies

This study describes an investigation using water lilies (*Nymphaea spontanea*) to remediate heavy metals (i.e. chromium and copper) from aqueous solutions and electroplating waste. Laboratory tests were conducted to evaluate the effect of different ages of water lilies in removing chromium and the efficiency of water lilies in accumulating different metal ions (i.e. chromium and copper) at various concentrations. Phytotoxicity tests on the test plants were also conducted to determine the plant tolerance towards these metal ions.

The absorption of metal ions by aquatic plants depends on the nature and the amount of aquatic plants, their stage of development, as well as the metal ion content and the presence of other dissolved substances. This study shows that plant age has significant effect on the removal and accumulation of chromium. Plants of 9 weeks old appeared to accumulate the most chromium followed by 6 and 3 weeks old plant. The roots of water lilies play an important role in the uptake of metal ions and the results show that metal accumulation in water lilies follow the order: roots > leaves > petioles. Water lilies are capable of accumulating substantial amount of chromium, up to 5956 μg/g, and copper, up to 10615 μg/g, and it is shown that copper is removed more rapidly than chromium. The preferential accumulation of copper over chromium is probably due to the selective nature of these plants and the chemical behaviour of the metal ions. Removal of metals by water lilies is more efficient when the metal is present singly in the solution than in mixed metal solution or waste solution. Results also show that copper is more toxic to water lilies when compared to chromium.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

PENYINGKIRAN Cu(II) DAN Cr(VI) DARIPADA PELBAGAI LARUTAN AKUAS OLEH BUNGA TERATAI (*NYMPHAEA SPONTANEA*)

Oleh

CHOO TZE PEI

Jun 2001

Pengerusi : **Profesor Lee Chnoong Kheng, Ph.D**

Fakulti: **Sains dan Pengajian Alam Sekitar**

Penyelidikan ini bertujuan untuk mengkaji potensi bunga teratai (*Nymphaea spontanea*) dalam bioremidiasi buangan logam berat umpamanya kromium dan kuprum. Ujian makmal telah dijalankan bagi menilai kesan peringkat kematangan bunga teratai dalam remidiasi kromium dan kecekapan bunga teratai untuk menyerap dan mengumpul pelbagai jenis ion logam dalam kepekatan yang berlainan. Ujian tosikologi logam ion terhadap bunga teratai juga dikaji bagi menentu ketahanan / toleransi tumbuhan terhadap logam–logam ion ini.

Penyerapan logam ion oleh tumbuhan akuatik adalah bergantung pada faktor-faktor seperti peringkat kematangan atau pertumbuhan dan logam ion yang didedahkan pada tumbuhan tersebut dan juga bahan yang terlarut dalam efluen buangan logam. Kajian ini telah menunjukkan peringkat kematangan tumbuhan yang berlainan

mempunyai keupayaan penyerapan dan pengumpulan logam ion yang berlainan. Tumbuhan yang berusia 9 minggu didapati berupaya mengumpul logam ion yang banyak sekali, dituruti tumbuhan yang berusia 6 dan 3 minggu. Akar bunga teratai memainkan peranan yang penting dalam peyerapan logam ion dan didapati dalam kajian ini, tren pengumpulan logam ion dalam bahagian-bahagian tumbuhan adalah seperti berikut: akar > daun > batang. Bunga teratai juga didapati berupaya mengumpul sebanyak 5965 μg/g logam kromium dan 10615 μg/g logam kuprum. Di samping itu, kajian ini juga menunjukkan bahawa lebih banyak logam kuprum dapat diremediasi daripada logam kromium. Ini mungkin disebabkan selektiviti tumbuhan tersebut terhadap logam ion yang tertentu dan juga sifat kimia logam ion tersebut. Kecekapan bunga teratai dalam penyerapan logam ion didapati lebih rendah dalam larutan yang mempunyai pelbagai jenis logam berbanding larutan yang hanya mempuyai sejenis logam dalamnya. Keputsuan-keputusan kajian ini juga mempamerkan bahawa logam kuprum adalah lebih toksik daripada kromium terhadap tumbuhan.

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I certify that an Examination Committee met on 7th June 2001 to conduct the final examination of Choo Tze Pei on her Master of Science thesis entitled "Removal of Cu(II) and Cr(VI) from Aqueous Solutions By Water Lilies (*Nymphaea spontanea*)" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

AINI IDERIS, Ph.D.
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Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

CHOO TZE PEI

Date: 13/06/01

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CHAPTER 1

INTRODUCTION

1.1 The Importance of Water

The recent water crisis in Malaysia, a country which is well-known for her water abundance, has led us to ponder on our mistake in thinking that water is an infinite resource. Water is an essential element, without which life cannot be sustained. In fact, water is uniquely fit as an environment for living things and provides millions of organisms with nourishment all the time. Thus, the role of water in nature is obvious. Man cannot live without water. Although there is growing recognition that instituting better water control is needed and that global water resources are limited and are rapidly becoming polluted, the full awareness of water as a precious and active element in nature has yet to be awakened.

1.2 Water Pollution

Water pollution has significantly become a major global problem. Concerns arise when man starts to realize that their "used to be" clean water is no longer safe to drink or play with. Contamination of water usually originates from pesticides runoff from agricultural land, industrial discharge into surface waters and urban runoff. These pollutants when interact with water may produce harmful effects to human, animal and plants.

The Minamata disease caused by mercury contamination in fish and the itai-itai disease due to ingestion of cadmium in water and food that occurred in Japan, are examples of severe health hazards caused by water pollutants (Yao, 1984). In addition, some of these pollutants are mutagenic and / or carcinogenic or have serious ecological implications (Esch, 1977).

1.3 Technologies for Wastewater Treatment

Generally water contaminants are subjected to treatments which involve reduction or elimination of suspended solids and particulate matter, both organic and inorganic. These processes also remove substances which are of nutritive value, such as nitrogen and phosphorous, as well as those that are toxic to organisms, such as heavy metals, pesticides and other organic compounds.

Presently, the main technologies which have been utilised to reduce or eliminate these pollutants include lime precipitation, ion-exchange, adsorption onto activated carbon, membrane processing and electrolytic methods. However, these conventional physical and chemical treatment procedures have been found to be limited, since they often involve high capital and operational costs. Furthermore, these methods are normally associated with the generation of secondary wastes which present treatment problems, for example, the large quantity of sludge generated by precipitation process (William *et al.*, 1998).

Nevertheless, the increasing demand for an improved environment has resulted in the search for better and cheaper wastewater treatment system. Bioremediation, a process that employs biological activity to mineralize organic contaminants or remove inorganic contaminants from polluted sites, has been gaining wide spread attention.

In this study, water lily (*Nympheae spontanea*), a natural filter in the aquatic system was tested for its potential for removing pollutants in industrial wastewater.

1.4 Objectives

The objectives of this study were as below:

- To determine the effectiveness of heavy metal removal by water lily.
- To study the effect of heavy metals towards plant growth.
- To study the effect of plant maturity on its removal of heavy metals.
- To evaluate the effectiveness of using water lily in the treatment of industrial wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Industrial Wastewater Pollution

2.1.1 Hazardous Waste

Wastewater discharged by industrial operations are in some cases among the worst sources of water pollution. These pollutants are normally associated with the problems of severe oxygen depletion and / or turbidity, in other word, high BOD (biological oxygen demand), sedimentation or high concentration of suspended solids and the presence of toxic substances or hazardous waste (Laws, 1993).

Hazardous waste production is a by-product of industrialization. With the increase in emphasis on high technology industries, hazardous waste production has become more significant and the range of wastes produced becomes more varied. In Malaysia, it was found that the total quantity of various types of hazardous waste in 1987 was 380,000 cubic meter per year, and this amount was predicted to be tripled or more in the coming years (Shafii, 1992).

Hazardous wastes which contain heavy metals have aggravated the problem of water pollution. The problem becomes complex when several metal ions are involved, forming metal chelation resulting in unpredictable physical and biological changes in the environment according to the industries involve. In fact, the damage is more direct, since poisons are involved.

2.1.2 Heavy Metals

Heavy metals are defined as metals which show a specific gravity > 4.5 g/mL (Outridge and Noller, 1991); or elements which under biologically significant conditions tend to exist as cations (Phipps,1976). However, this term is often used where there are connotations of toxicity. Cadmium, copper, nickel, lead, chromium and mercury are most important heavy metal water pollutants. Some of these heavy metals (e.g. copper, zinc and iron) are essential micronutrients to plants and human, but others such as mercury, lead and cadmium have no known biological function. Virtually, all metals including the essential metal micronutrients, are toxic to aquatic organism as well as humans, if exposure levels are sufficiently high. Table 2.1 gives some idea of relative toxicity of various metals based on the maximum permissible concentrations in water recommended by the Environmental Protection Agency (EPA) for the protection of human health.

Since heavy metals are elements, they cannot be degraded once released. Despite this, heavy metals are not environmentally "constant" when released, but rather may be affected in several ways. For instance, biological and physical forces in the environment can change the chemical form of the heavy metals. This means interconversion between organic and inorganic forms of the metals, or changes in the organic forms. Due to these changes, there is a marked difference in the reactivity of the heavy metals with biological and non-biological sites in the environment, thus resulting in uncertainties for scientists and regulatory officials in assessing the environmental consequences of increase in the heavy metal burden.

Table 2.1 Maximum permissible concentrations of various metals in natural waters for protection of human health

		Maximum Permissible Concentration	
Metal	Chemical symbol	mg/L	µM/L
Mercury	Hg	0.144	0.72
Lead	Pb	5	24
Cadmium	Cd	10	89
Selenium	Se	10	127
Thallium	Tl	13	64
Nickel	Ni	13.4	228
Silver	Ag	50	464
Manganese	Mn	50	910
Chromium	Cr	50	962
Iron	Fe	300	5372
Barium	Ba	1000	7281

Source: EPA (1987)

The fact that heavy metals have been present in some parts of the environment for millennia is recognized. Metals are introduced naturally into aquatic system as a result of the weathering of soils and rocks, and from volcanic eruptions. However, a more important source of increased heavy metal concentration is the by-products of modern society. Mining and mineral processing, fossil fuel combustion, the dumping and burial of industrial waste, car fumes, domestic waste discharge are few examples of ways in which modern society may alter the environment (Manahan, 1994).

2.1.2.1. The Toxicity and Effect of Heavy Metals

The toxicity of heavy metals, manifested in aqueous solution may be expressed through acute poisoning, teratogenicity, mutagenicity, or carcinogenicity (Stoner, 1993). A metal toxicant may bring about one or more of these effects. If more than one is exhibited, then the effects are likely dose dependent. Metal toxicity may affect all forms of life including microorganisms, plants and animals, but the degree of toxicity varies for different organisms.

The effect of heavy metals on the environment depends on the concentrations of the heavy metals and their chemical forms. Heavy metals are particularly toxic in their chemically combined forms and some, notably mercury, are toxic in the elemental form (Manahan, 1994). For a single element, the concentration of direct importance may be that fraction of the total which is available to be mobilized by physical forces such as wind, water, or soil, and the partition of this form among the physical and biological constituents of the environment.

Even when the concentration of metal toxicant may be below the permissible concentration, the presence of this substance may, nevertheless, constitute a health hazard due to the phenomenon of bioaccumulation (Stoner, 1993). A metal toxicant may be accumulated and concentrated within a single organism by ingestion over time or through successive trophic levels in a food chain. These cumulative effect are dependent on the fixation of the toxic substance in the organism involved or on the absence of significant excretion at any trophic level. In addition, chemical interconvertion also contributes to significant change in the concentration of the metal in a given locale. Unavoidable mobilization of heavy metals that results from leaching of ores by rain or running water is a good example to describe this occurrence.

Increasing contamination of the aquatic environment by heavy metals posed a serious threat to biota (Forsthner and Wittmann, 1979). The presence of heavy metals in the environment can be detrimental to a variety of living species, including man. Heavy metals produced undesirable effects, even if they were present in